

# THE DISTRIBUTION OF SOLUTE PROCESSES ON AN ACID HILLSLOPE AND THE DELIVERY OF SOLUTES TO A STREAM: I. EXCHANGEABLE BASES

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## ABSTRACT

This paper aims to identify the spatial distribution of exchangeable base cations in soils on an acid hillslope and to investigate possible cation release processes from slope soils to the stream. The basic assumption underlying this research is that the amount of exchangeable cations in soils reflects the nutrient stores and cation leaching processes across the slope where vegetation and parent materials are similar. The distribution of exchangeable  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^{+}$  and  $\text{Na}^{+}$  has been investigated on a three-dimensional hillslope on the Quantock Hills, Somerset, UK. A two-way ANOVA shows that soil depth is predominant in explaining the total variance of exchangeable bases, despite the steep slope gradient and clear podzolic catena development. Major nutrient base cations, such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{K}^{+}$ , display homogeneous topsoil storage right across the slope. This spatial pattern may indicate that the spatial distribution of major nutrient cations is tightly controlled by the soil–vegetation system in nutrient-poor heathland environments.  $\text{Na}^{+}$  is an exception to this vegetation-controlled spatial distribution, because of its small involvement in the soil–vegetation and soil exchangeable systems. In subsurface soils, cations liberated from the soil–vegetation system are subject to redistribution over the slope according to the hydrological flowpaths operating on the slope, with some eventually released into the stream. The saturated wedge developed at the base of the slope plays a key role in the storage and release processes of base cations from slope soils to the stream.  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Na}^{+}$  carried by throughflow are stored in the saturated wedge and gradually released into the stream at times of high flow.  $\text{K}^{+}$ , however, shows an apparently different spatial behaviour, being deficient in the saturated wedge. Copyright © 1999 John Wiley & Sons, Ltd.

KEY WORDS: spatial variability; catena; base cations; throughflow; saturated wedge

## INTRODUCTION

Stream-water chemistry is mainly controlled by the spatial variation of solute processes associated with biotic and pedogenic processes over hillslopes, and by element transformation processes which may result in the transfer of solutes from slope soils to streams. Various field investigations have shown that the spatially differentiated physico-chemical properties of soils on hillslopes may play a central role in the determination of water quality (e.g. Hill, 1990; Mulder *et al.* 1991; Chappell and Ternan, 1992; Billett and Cresser, 1992). In addition, some geomorphologists have emphasized the importance of the spatial variation of solute processes in the determination of chemical denudation rates over hillslopes (Burt, 1986; Trudgill *et al.*, 1996). Recently, the need for quantification and modelling of soil variability at the hillslope scale, especially in association with assessments of land quality and environmental protection, has also been addressed (Hoosbeek and Bryant, 1992; Moore *et al.*, 1993). Despite strong interest, however, remarkably little progress has been made in the actual identification of the spatial variation of solute processes over a hillslope and its spatial connection with the stream.

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In this paper, we examine the spatial distributions of exchangeable bases ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^{+}$  and  $\text{Na}^{+}$ ) on a three-dimensional hillslope and their possible connection with the hydrochemical response of the stream. The mass balance of base cations has been intensively studied in various catchments for the quantification of catchment-scale nutrient cycles and chemical weathering (e.g. Johnston *et al.*, 1969; Cleaves *et al.*, 1970; Waylen, 1979; Paces, 1986). During the course of such studies, one commonly posed question is how to incorporate the spatial variability of hydrological and geochemical processes into the results of mass balance relationships (Trudgill, 1986). Monitoring the spatially distributed flow pathways and chemistry of soil water may be the most direct means to tackle this problem. However, given the time involved in field monitoring in relation to seasonal or short-term changes in soil water chemistry, it becomes very expensive to collect and analyse soil water. The assumption made in this research is that the cation exchange properties of soils will reflect solute processes operating across hillslopes (Trudgill, 1988). Cation exchange responds quickly to changes in soil solution chemistry, and the ratios of exchangeable cations at soil exchangeable sites reflect the ratios of cation concentration in soil solution (Furrer *et al.*, 1989).

The specific objectives of this paper are: (1) to understand the spatial variability of exchangeable bases on an acid, nutrient-poor hillslope; (2) to visualize the spatial distribution of exchangeable bases in terms of the nutrient store and solute processes; and (3) to infer the hydrochemical release processes of such bases from slope soils into the stream. A second paper (Park and Burt, 1999) investigates the spatial distribution of exchangeable  $\text{Al}^{3+}$  and Al oxides over the hillslope in order to identify Al leaching processes from a highly acidified hillslope to a stream.

## STUDY SITE

The study area is a small south-facing slope (100 m  $\times$  300 m) at Bicknoller Combe on the Quantock Hills in Somerset, UK (Figure 1). The overall hillslope profile shows the progression: flat interfluvial – convex slope – steep straight slope – (weak) concave foot slope (Figure 1). The straight valley sides have an average slope angle of about 23° throughout the catchment, though this reduces to 20° at the base of the hollow, and approaches 30° on the lower spurs. The hollow extends upslope from the base of the slope almost reaching the flat interfluvial. There are two springs at the base of the hollow, forming a seepage zone. The three-dimensional arrangement of the hollow and spurs governs hydrological flowpaths, and in turn strongly influences slope denudation and soil development (Anderson and Burt, 1978; Crabtree and Burt, 1983; Park *et al.*, 1996). Two meteorological stations at different altitudes (96 m OD and 286 m OD) at Nettlecome Court Field Centre (ST 057377), about 6 km southwest from Bicknoller Combe, indicate the general climate of this locality. Average annual rainfall is 985 mm at the lower site and 1080 mm at the higher site. Mean air temperatures at the two sites are 9.6°C and 8.9°C respectively.

The slope is covered by the deep (>2 m) and stratified regolith of the Hangman Grits of the Middle (or Late) Devonian. The Hangman Grits consist mainly of fine- or fine- to medium-grained, strong, thickly bedded or massive sandstones with frequent subordinated shales, siltstone and mudstone strata (Edmonds and Williams, 1985). The composition of rock fragments indicates a general uniformity of parent materials, and two principal characteristics in relation to pedogenesis: relatively high resistance to weathering and low base content. Figure 1 shows the spatial distribution of a podzolic catena identified on the study slope. Detailed descriptions of soil morphology may be found in Park *et al.* (1996).

The study slope is used as rough grazing for sheep. On the flat interfluvial the vegetation is dominated by bent-fescue grass (*Agrostis-Festuca*) and patches of gorse (*Ulex europaeus*) and cross-leaved heath (*Erica tetralix*). Approaching the convex shoulder slope, bristle bent (*Agrostis setacea*) and bilberry (*Vaccinium myrtillus*) appear. Bracken (*Pteridium aquilinum*) is dominant over large parts of the upper and middle slope. Heaths and grass also occur in the bracken-dominant area, but they are very scattered and their extent is limited. The bracken area changes to a mixed grass and bracken community on the lower parts of the slope. In the seepage zone in the lower hollow, locally there are sedges (*Carex* spp.) and rushes (*Juncus* spp.), and abundant nettle (*Urtica urens*).

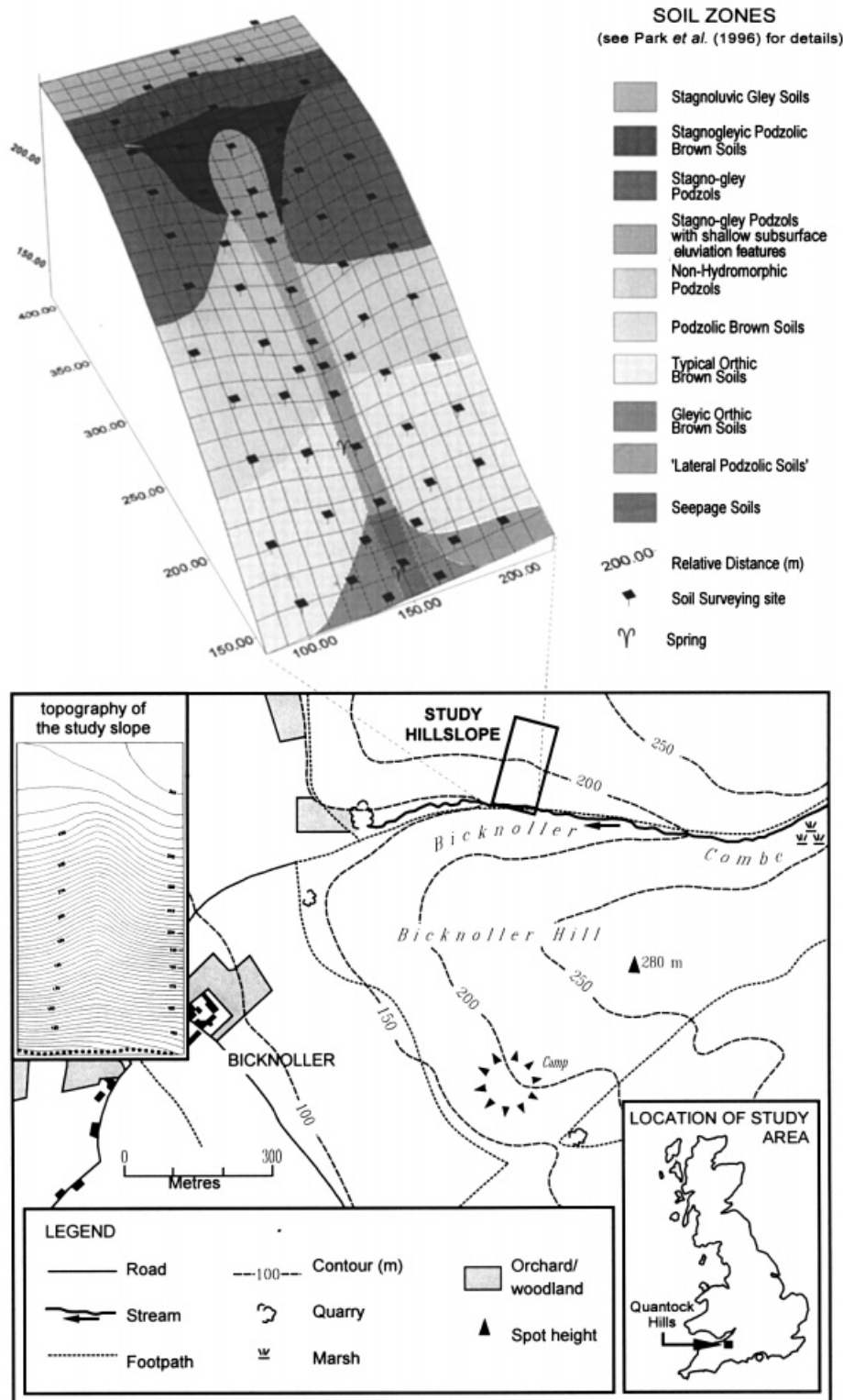


Figure 1. The location of the study site in Bicknoller Combe, the Quantock Hills, Somerset, and a podzolic catena development on the study slope

Table I. Descriptive statistics of soil chemistry in the study slope, Bicknoller Combe, the Quantock Hills, Somerset

Soil variables	Mean	Range		St dev.	CV*	Two-way ANOVA			
		Min.	Max.			Profile (a)†	Depth (b)†	a/b	R <sup>2</sup>
pH*	3.23	2.18	5.61	0.52	8.11	28.08	145.65	0.19	0.87
Clay content (%)*	8.30	3.31	17.99	2.16	13.20	5.98	8.51	0.70	0.51
Loss-on-ignition (%)*	5.51	0.62	39.94	3.57	32.46	6.33	35.85	0.18	0.63
Exchangeable cations (mg kg <sup>-1</sup> )‡									
Ca <sup>2+</sup>	87.02	2.40	4508.45	268.32	29.35	17.86	81.83	0.22	0.82
Mg <sup>2+</sup>	23.54	0.54	1451.80	89.43	42.63	18.92	88.04	0.22	0.83
Na <sup>+</sup>	8.78	1.64	112.62	7.77	25.59	13.36	31.59	0.42	0.73
K <sup>+</sup>	50.70	4.10	356.14	48.88	22.65	21.16	181.52	0.12	0.87
Al <sup>3+</sup>	277.88	3.67	1104.97	170.92	32.34	8.92	14.86	0.60	0.62
TEB (mmol <sub>c</sub> kg <sup>-1</sup> )‡	7.96	0.71	357.20	21.46	52.39	21.14	109.38	0.19	0.85
ECEC (mmol <sub>c</sub> kg <sup>-1</sup> )‡	39.31	3.41	358.72	25.52	14.67	6.98	13.59	0.51	0.59
Base saturation (%)‡	19.01	1.46	99.74	19.80	36.16	18.51	69.73	0.27	0.81

TEB, total exchangeable bases; ECEC, effective cation exchange capacity; CV, coefficient of variation.

ECEC has been calculated in moles of charge of exchangeable cations (mmol<sub>c</sub> kg<sup>-1</sup>) by the summation of seven (Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, Al<sup>3+</sup>, Fe<sup>3+</sup> and Mn<sup>2+</sup>) extracted exchangeable cations (Amacher *et al.*, 1990).

\* Square root transformation

† Significance level of F-ratio ( $p < 0.01$ )

‡ Logarithm (base 10) transformation

## METHODS

Soil samples were collected from 64 soil profiles based mainly on a 25 m sampling grid (Figure 1). Pits varied in depth from 50 cm to 110 cm depending on the stoniness of the subsoil. Detailed soil morphology is described in Park *et al.* (1996). Soil samples of *c.* 2 kg were collected for laboratory analysis at a 10 cm sampling interval. Even-depth sampling was selected for two reasons: (1) the main interest of this research is the vertical comparison of each soil profile; (2) lateral continuity of soil horizonation is poor because of coarse soil textures and high slope angle.

The 502 samples collected were dried at room temperature and gently ground to pass a 2 mm sieve. Soil pH was measured in 0.01 M CaCl<sub>2</sub> solution in 1:2.5 ratio (*w:v*). Organic content was estimated by using low temperature ashing at 375°C for 16 hours. The weight proportion of clay was estimated by using a laser granulometer after sequential extraction of organic materials with H<sub>2</sub>O<sub>2</sub>, and oxides and hydroxides with dithionite-citrate-bicarbonate solution. Exchangeable bases (Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup> and Na<sup>+</sup>) and other exchangeable cations (Al<sup>3+</sup>, Fe and Mn) are measured using an atomic absorption spectrophotometer after a single-step extraction using 0.1 M BaCl<sub>2</sub>–NH<sub>4</sub>Cl<sub>2</sub> solution, as specified in Amacher *et al.* (1990). Since a large number of samples was used in this research, the precision of each measurement was assessed using duplicated and triplicated measurement of some randomly selected samples. The coefficient of variation of the repeated measurements was 1.3 per cent for soil pH, 4.3 per cent, for loss-on-ignition, 8.5 per cent for exchangeable Ca<sup>2+</sup>, 4.2 per cent for Mg<sup>2+</sup>, 2.9 per cent for K<sup>+</sup>, 5.7 per cent for Na<sup>+</sup>, and 2.9 per cent for Al<sup>3+</sup>.

Soil variables which do not show a normal distribution have been transformed (Table I). Total variability of each soil attribute is assessed by calculation of the coefficient of variation (CV). It is well known that many different environmental factors are involved in the total variability of soil attributes (e.g. Beckett and Webster, 1971; Wilding, 1984). The main concern in this research, however, is to assess the influence of lateral and vertical components on total variability of soil attributes on the study slope. Soil properties in natural landscapes vary not only with location but also with depth, but little work has been done to identify these vertical and lateral differences in the variance structure of soil attributes at the hillslope scale (Wilding, 1984). The total variance of each soil attribute measured may be subdivided into three components: the sums of squares due to lateral variation (sampling position), the sums of squares due to vertical variation

(sampling depth), and the remainder. The effect of these components can be assessed by unbalanced two-way analysis of variance without replication (Milliken and Johnson, 1984). While ANOVA procedures are primarily used for experimental hypothesis testing, they can also provide a way of assessing sources of variation (Milliken and Johnson, 1984). Owing to practical constraints, the soil sampling depth rarely reaches more than 1 m and the possible interaction between lateral and vertical components and measurement error cannot be estimated. Therefore the results of this analysis should be limited to the relative assessment of lateral and vertical components to total soil variation. Two-way ANOVA procedures were performed in SPSS MANOVA following the unbalanced random model. The F-ratios for each factor were determined by the ratio of the mean square of each factor to the mean square of the remainder, and the 'goodness of fit' of the model was assessed by  $R^2$ , using SPSS (Table I).

In order to compare the level of exchangeable bases between soil zones at each soil sampling depth, a one-way ANOVA test is used. The ten soil zones shown in Figure 1 are reduced to seven soil zones (orthic brown soil (OBS); podzolic brown soils (PBS); non-hydromorphic podzols (NP); stagnogley podzols (SP); stagnogley soils (SLG); 'lateral podzolic soils' (LPS); and seepage soils (SS)) for the statistical comparison, by disregarding subzones and merging stagnoluvic gley soils and stagnogleyic podzolic brown soils into stagnogley soils. The seepage soil zone is omitted from the ANOVA test, because soil samples collected from seepage soils frequently show extreme values for many of the soil properties examined. In order to identify which groups have significantly different means, the Bonferroni test is used using SPSS.

Maps for each soil attribute are drawn by using a linear kriging at five soil depths (0–10 cm, 20–30 cm, 40–50 cm, 60–70 cm and 80–90 cm depth). The number of sampling sites varies from 48 to 64. We could not collect samples from below 60 cm depth at the base of the hollow (groundwater saturation) and on the interfluvium (dense subsurface layers). There was no consideration of nugget effect or zonal anisotropy in the actual interpolation procedure, because serious zonal anisotropy in the experimental semivariograms and limited sampling points made it difficult to construct an accurate variogram model for the kriging.

## RESULTS

### *Variability of exchangeable bases*

The soil at the study site is a very stony, sandy silty loam. Average soil pH measured in 0.01M CaCl<sub>2</sub> solution is 3.23, ranging from 2.18 to 5.16 (Table I). Such high soil acidity seems to be caused by the low level of soluble and weatherable materials in the parent materials. The nature of the parent materials – coarse-textured soils and quartzitic sandstones – determines the low effective cation exchange capacity (ECEC) of the soils studied (average 39.31 mmol<sub>c</sub> kg<sup>-1</sup>). Exchangeable bases are highly variable: CV is 29.35 per cent for Ca<sup>2+</sup>, 42.63 per cent for Mg<sup>2+</sup>, 22.65 per cent for K<sup>+</sup>, and 25.59 per cent for Na<sup>+</sup> (Table I). Total exchangeable bases (TEB) and base saturation (BS) show even higher variability (52.35 per cent for TEB and 36.16 per cent for BS). This is a similar result to those found in other studies (Ball and Williams, 1968; Beckett and Webster, 1971; Wilding, 1984). On the other hand, ECEC shows a low total variability (CV = 14.67 per cent).

The total variance of exchangeable cations, except Al<sup>3+</sup>, is well explained by the two-way ANOVA model, with goodness of fits ( $R^2$ ) of 0.7–0.8. Considering the relatively similar vegetation and parent materials at the study slope, the two-way ANOVA model gives a clear view of the variance structure of exchangeable bases. All F-ratios, both in profile and depth components, have a sufficiently low significant level (< 0.01) to reject the null hypothesis. Thus, the ratio between F-ratios for soil profile and depth indicates the relative contribution of components to total variance of exchangeable cations. Most exchangeable bases and other basic soil attributes clearly show that F-ratio for sampling depth is much higher than that for the sampling location. K<sup>+</sup> has the clearest vertical differentiation among the exchangeable bases, followed by Ca<sup>2+</sup> and Mg<sup>2+</sup>, which have virtually the same variation characteristic. It is inferred that vertical pedogenesis may provide a stronger influence on the variability of exchangeable cations than various catenary soil differentiation processes, despite the high slope angle and complex development of soil types on the study slope. The few exceptions are exchangeable Al<sup>3+</sup>, ECEC and clay content, all with relatively low  $R^2$  values. Their spatial distribution is described in detail in Park and Burt (1999).

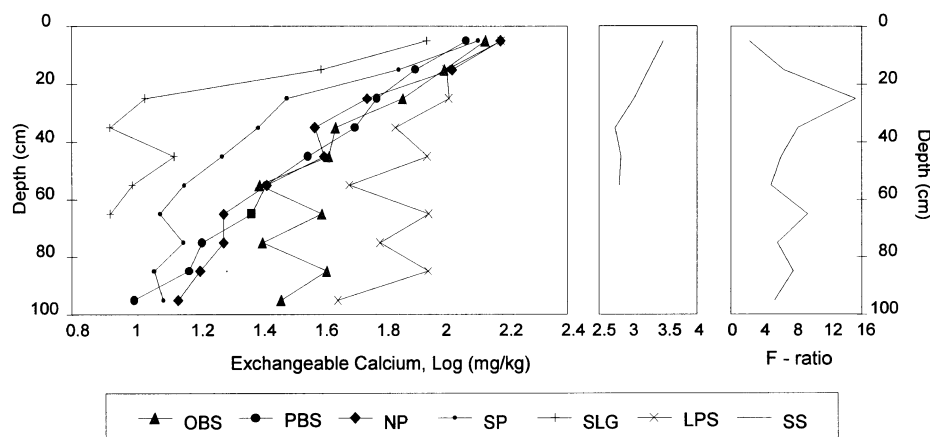


Figure 2. Vertical comparison of exchangeable calcium between seven different soil zones in Bicknoller Combe, Somerset. Total soil profiles ( $n = 64$ ); OBS (orthic brown soils,  $n = 14$ ); PBS (podzolic brown soils,  $n = 13$ ); NP (non-hydromorphic podzols,  $n = 12$ ); SP (stagnogley podzols,  $n = 13$ ); SLG (stagnogley soils,  $n = 8$ ); LPS ('lateral podzolic soils',  $n = 5$ ); SS (seepage soils,  $n = 2$ )

Table II. F-ratio in the multiple comparison of exchangeable soil attributes between six soil zones in the study slope, the Quantock Hills, Somerset

Depth (cm)	Exchangeable $\text{Ca}^{2+}$		Exchangeable $\text{Mg}^{2+}$		Exchangeable $\text{K}^{+}$		Exchangeable $\text{Na}^{+}$	
0–10 ( $n = 58$ )	2.28*	0.0604†	1.08	0.3843	2.76	0.0275	1.93	0.1040
MC‡						4 ↔ 1		
20–30 ( $n = 64$ )	15.22	0.0000	19.59	0.0000	8.97	0.0000	9.86	0.0000
MC		4 ↔ 0,1,2,3,5		4 ↔ 0,1,2,3,5		4 ↔ 0,1,2,5		4 ↔ 0,1,2
		3 ↔ 0,5		3 ↔ 0,1		3 ↔ 5		3 ↔ 0,1
40–50 ( $n = 64$ )	6.13	0.0001	8.08	0.0000	4.97	0.0007	3.18	0.0129
MC		4 ↔ 0,2,5		4 ↔ 0,1,2,5		4 ↔ 1,2,5		4 ↔ 0,1,2
		3 ↔ 5		3 ↔ 0,5		3 ↔ 5		
60–70 ( $n = 59$ )	9.36	0.0000	12.23	0.0000	5.63	0.0003	3.27	0.0114
MC		0 ↔ 3,4		0 ↔ 2,3,4		5 ↔ 0,2,3,4		4 ↔ 5
		5 ↔ 1,2,3,4		5 ↔ 1,2,3,4				
80–90 ( $n = 48$ )	7.64	0.0000	9.05	0.0000	3.60	0.0080	1.55	0.1936
MC		0 ↔ 1,3		0 ↔ 1,2,3		3 ↔ 5		
		5 ↔ 1,2,3		5 ↔ 1,2,3				

\* F-ratio in one-way ANOVA

† Probability in one-way ANOVA

‡ Multiple comparison of soil zones (Bonferroni test): 0, orthic brown soils; 1, podzolic brown soils; 2, non-hydromorphic podzols; 3, stagnogley podzols; 4, stagnogley soils; 5, 'lateral podzolic soils' (see Figure 1 and Park *et al.* (1996) for details)

### Exchangeable $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$

The mean concentrations of exchangeable  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are  $87.02 \text{ mg kg}^{-1}$  and  $23.54 \text{ mg kg}^{-1}$  respectively (Table I). This makes them the second and fourth most abundant exchangeable cations in the study soils. Only exchangeable  $\text{Ca}^{2+}$  will be examined here, because exchangeable  $\text{Mg}^{2+}$  shows a similar spatial distribution with exchangeable  $\text{Ca}^{2+}$  in the study soils ( $r = 0.94$ ;  $p < 0.01$ ). While there is some degree of difference in biological involvement, they behave in a similar fashion, especially in a heathland ecosystem (Gimingham, 1972; Duchaufour, 1982).

In vertical distributions, the average concentration of exchangeable  $\text{Ca}^{2+}$  decreases rapidly with depth (Figure 2). This decrease is accompanied by an increase in total variability from 14 per cent to 30 per cent. The F-ratio indicates that a soil grouping based on morphological patterns has limited meaning in the top 10 cm of soils for exchangeable  $\text{Ca}^{2+}$  (2.28), although the F-ratio significantly increases between 20 cm and 40 cm depth (15.2–6.2; Table II). The increase in F-ratio is mainly due to the difference between stagnogley soils and other soil zones.

The seven soil zones can be roughly divided into four types of vertical sequence. Soil samples collected from seepage soils have a remarkably high concentration of exchangeable  $\text{Ca}^{2+}$ . Other soil zones show similar levels in topsoil, but different levels in subsurface layers. Orthic brown soils and 'lateral podzolic soils' form the second group with a unique vertical sequence: concentration decreases below the topsoil, and then becomes very variable. Compared to other soil zones, the concentration in subsurface soil layers is significantly higher. The third group includes stagnogleyic podzols and stagnogley soils, which have relatively low concentrations with a steep decrease with depth. These two soil zones are subject to strong chemical leaching by shallow subsurface flow with little influx of divalent cations from upslope. The last group includes podzolic brown soils and non-hydromorphic podzols, which show a steady decrease with depth. Orthic brown soils follow the same sequence at shallow soil depths.

In the interpolated maps, levels of exchangeable  $\text{Ca}^{2+}$  in surface soils are uniform, except in the lower hollow and on the western part of the interfluve (Figure 3A). The even distribution of divalent cations over most of the slope is a remarkable result, considering the various complicating pedogenic and geomorphological processes operating on the study slope, which leads to differences in many other soil properties (Park, 1997), and the catenary development of soil types. It indicates that none of the catenary differentiation processes have significant influence on the level of exchangeable  $\text{Ca}^{2+}$  in topsoil.

The homogeneous level of exchangeable  $\text{Ca}^{2+}$  in topsoil may reflect a tight soil-vegetation system in the study slope: Ca and Mg are important nutrients for plant growth, and they never pass straight through a soil system without biological involvement (Duchaufour, 1982). A given year's net primary production includes a large proportion of mineral nutrients recycled from the decay of the previous year's litter. In terms of initial supply of these cations, atmospheric input may have a significant role at the study site, given the low content of weatherable primary minerals in bedrock; it is often argued that atmospheric deposition is one of the main sources of the base nutrient cations in nutrient-poor heathland (Gimingham, 1972; Trudgill, 1988). The geographical location of the study slope next to the Bristol Channel and the prevailing westerly winds may provide a large amount of soluble cations for the slope. Whilst there is active leaching, especially through A horizons in which a dense bracken rhizome network is developed and hydraulic conductivity is much higher than in B horizons (Park *et al.*, 1996), continuous supply of cations by atmospheric input and litter fall maintains uniform levels of divalent cations in topsoil right across the slope.

The exchangeable  $\text{Ca}^{2+}$  maps for deeper soil layers do, however, show some clear catenary distribution (Figure 3B-E): low levels of exchangeable  $\text{Ca}^{2+}$  occur upslope at 20–30 cm depth, but they gradually increase downslope with depth. At greater depths, the high levels of exchangeable  $\text{Ca}^{2+}$  in the lower parts in the hollow are accentuated and extend upslope along the hollow and lower parts of the downstream spur. The gradual increase in divalent cations along the slope profile is slightly distorted at the base of the downstream spur where levels are relatively low. The gradual increase in exchangeable  $\text{Ca}^{2+}$  with depth at lower slope positions can be explained by hydrological processes operating on the study slope. The upslope region is subject to active geochemical leaching by subsurface throughflow. Low exchangeable  $\text{Ca}^{2+}$  content with depth in the upper parts of slope is presumably caused by the increased effect of leaching in zones of limited upslope area. The leached divalent cations are carried by throughflow down towards the base of the slope.

One immediate question that arises is whether the gradual increase in divalent cations downslope is due to the accumulation of leached cations from upslope or to less intense chemical leaching. Before answering this question, it should be noted that there are two different hydrological processes downslope, and these may be closely connected with the general distribution of divalent cations in this part of the hillslope. The downslope spurs can be defined by the predominance of vertical leaching in the absence of clear impeding pedogenic layers (Park *et al.*, 1996). While this is complicated by the stratification of parent materials, lateral connection with upslope areas along the flanks and spurs appears weak. Furthermore, considering the general slope configuration and the low concentration of solutes in the soil and stream waters, it is hard to argue that there is an accumulation of leached cations from upslope in this part of the slope. Therefore, the high level of divalent cations in the spurs seems to be caused by less intense chemical leaching. In the case of the lower hollow and flanks, however, a different process appears to maintain the higher level of exchangeable cations. This area is under the continuous influence of throughflow in the form of a saturated wedge (Anderson and Burt, 1978), whose position is roughly concordant with the spatial arrangement of seepage soils and gleyic orthic brown

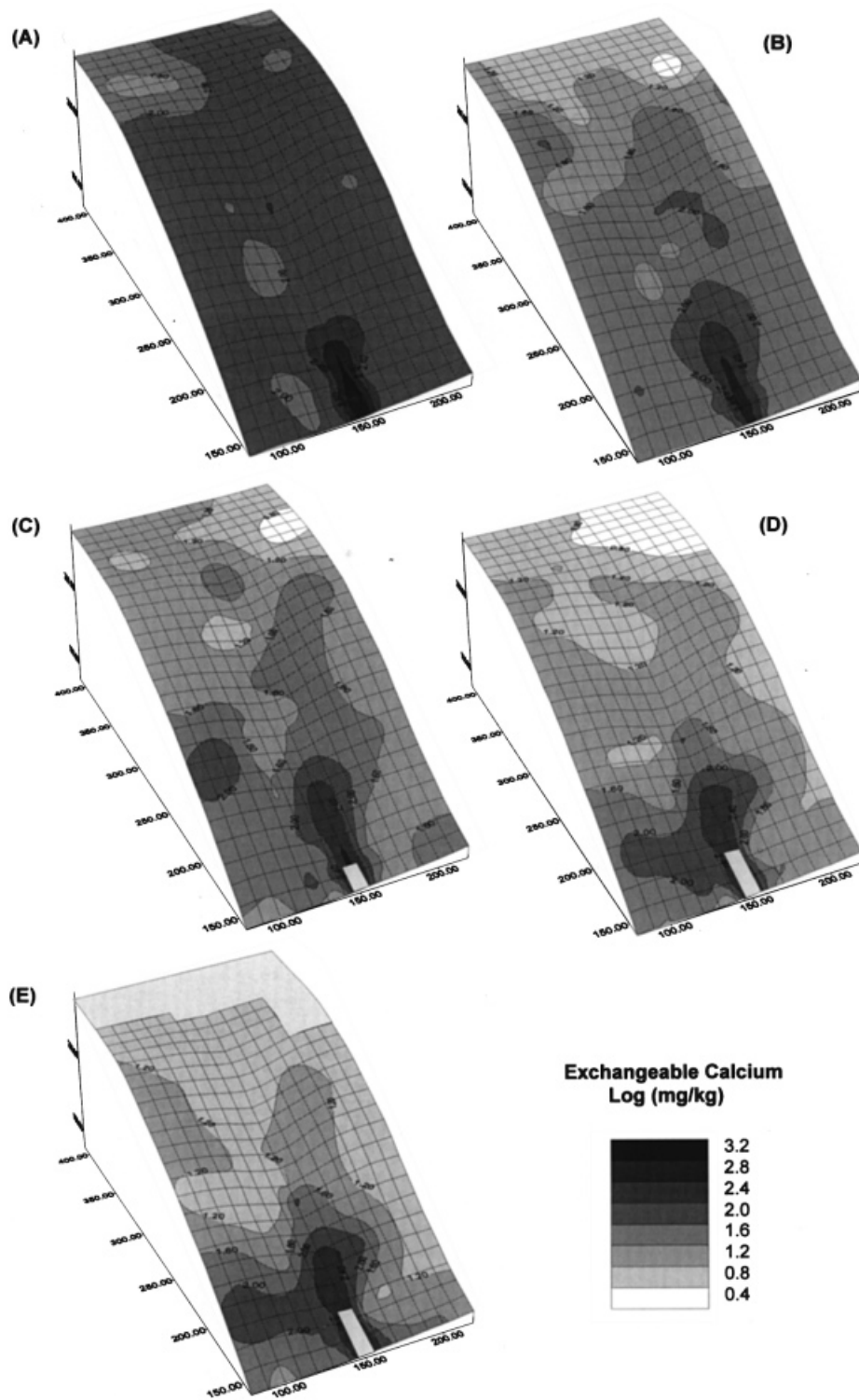


Figure 3. Spatial interpolation of exchangeable calcium in five soil layers in Bicknoller Combe, Somerset. (A) 0–10 cm depth ( $n = 64$ ); (B) 20–30 cm depth ( $n = 64$ ); (C) 40–50 cm depth ( $n = 62$ ); (D) 60–70 cm depth ( $n = 59$ ); (E) 80–90 cm depth ( $n = 48$ )



soils (Figure 1). This division of geochemical processes in the lower slope is accordant with conclusions made on the study slope by Burt (1979). He differentiated two distinct chemical erosion environments in the lower slope: on the spurs, leaching seemed to be related solely to infiltration processes, whilst in the hollow, throughflow also contributed to solute removal.

Within individual soil profiles, the increase in exchangeable  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , which is frequently associated with a decrease in exchangeable  $\text{Al}^{3+}$ , is observed in the water-saturated parts of seepage soils, gleyic orthic brown soils, and some typical orthic brown soils. Figure 4 compares the vertical distribution of exchangeable divalent cations and exchangeable  $\text{Al}^{3+}$  for four soil profiles surveyed on the lower slope. In seepage soils, exchangeable  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  show high concentrations, whilst exchangeable  $\text{Al}^{3+}$  usually shows low concentrations (Figure 4A). Although the water table was directly observed in only two soil profiles at the base of the slope, water saturation in the lower parts of the soil profiles due to the capillary rise from the water table was common (Park *et al.*, 1996). The vertical trend of exchangeable divalent cations in these soil profiles shows a 'C' shape, decreasing immediately below the topsoil, then increasing again in the water-saturated parts (Figure 4B and C). This pattern has been observed in all gleyic orthic brown soils and some orthic brown soils, and is in contrast to the gradual decrease in divalent cations in typical orthic brown soils (Figure 4D).

The high level of divalent cations in the lower parts of the hollow may well be associated with the influence of convergent throughflow. The incoming waters in this area carry higher divalent cation concentration due to long residence time, with cations leached from upslope. The divalent cations carried by convergent throughflow may be partly adsorbed to cation exchange sites in the water-saturated parts of soils in the base of the hollow. The unstable 'zig-zag' shape of cation distributions in these soil profiles (Figure 2) may partly reflect the different depths at which high concentrations of these cations occur. However, the relative importance of less advanced acidification and absorption is difficult to quantify.

#### *Exchangeable potassium ( $\text{K}^+$ )*

The mean exchangeable  $\text{K}^+$  is  $50.7 \text{ mg kg}^{-1}$ , and it is the third most abundant exchangeable cation by weight after exchangeable  $\text{Al}^{3+}$  and  $\text{Ca}^{2+}$ . The average concentration of exchangeable  $\text{K}^+$  decreases with depth, although at a reduced rate below 50 cm (Figure 5). Two-way ANOVA shows that exchangeable  $\text{K}^+$  shows the clearest vertical difference among 32 soil variables considered in the study slope (Park, 1997). It is widely known that bracken, the dominant species on the study slope, plays an active role in the potassium cycle (Frankland, 1976; Williams *et al.*, 1987). In an examination of cationic composition of throughfall, stemflow and litterflow under bracken on Dartmoor, Williams *et al.* (1987) showed that  $\text{K}^+$  is the dominant cation in throughfall and stemflow, and there is a sixfold increase in  $\text{K}^+$  concentration in litterflow compared to throughfall and stemflow.

As with divalent cations, the F-ratio at 20–40 cm depth is slightly higher than above or below, but generally the difference in exchangeable  $\text{K}^+$  between different soil zones is small (Table II). While stagnogley soils and seepage soils each show distinctive vertical distributions, the soil zones developed along the main slope segment resemble each other. Unlike the divalent cations, exchangeable  $\text{K}^+$  is not observed to increase in the water-saturation zone downslope; indeed, the opposite may be true. The concentration of exchangeable  $\text{K}^+$  in the topsoil of seepage soils is slightly higher than in any others, but it decreases rapidly with depth, only stagnogley soils recording lower levels at depth. The orthic brown soils also show lower concentrations than the upslope podzolic soils. The concentration of exchangeable  $\text{K}^+$  in orthic brown soils drops continuously with depth, and is lowest in the deep subsurface layers (80–100 cm depth). While an unstable vertical sequence between 30 and 90 cm depth is obvious in 'lateral podzolic soils', the main water-saturated horizons (90–100 cm) show low concentrations.

Maps of exchangeable  $\text{K}^+$  (Figure 6) show that the highest concentration in topsoil occurs on the middle and lower slope, including the lower hollow. While there is some spatial patterning, such as low levels on the upper parts of slope and high levels in the lower hollow upslope of the seepage soil zone, the distribution is rather poorly defined. Clear catenary differentiation, as shown in the case of exchangeable  $\text{Ca}^{2+}$ , can barely be detected. One notable difference compared with exchangeable  $\text{Ca}^{2+}$  and  $\text{Na}^+$  is that exchangeable  $\text{K}^+$  shows a lower concentration in the lower hollow than on the adjacent spurs in the deeper soil layers (20–

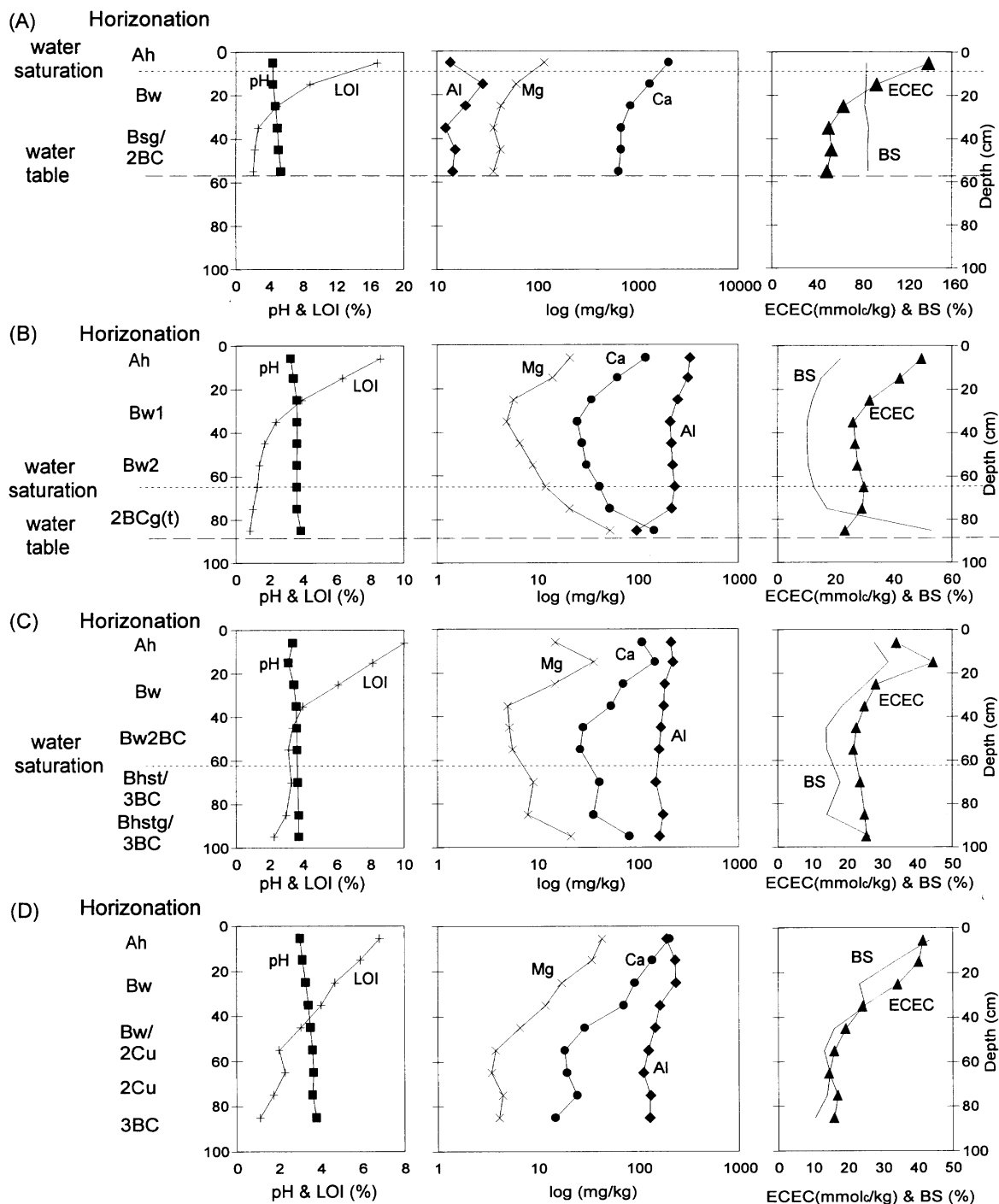


Figure 4. Some representative soil profiles for understanding the increase of divalent exchangeable cations ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) and consequent increase of base saturation at the water saturation part of the soil profile. The approximate water saturation limit is shown, which is defined as some sticky feeling of fine materials. (A) Profile 2-3 (seepage soil); (B) profile 0.5-3.5 (gleyic orthic brown soil); (C) profile 1-4 ('lateral podzolic soil'); and (D) profile 3-5 (typical orthic brown soil)

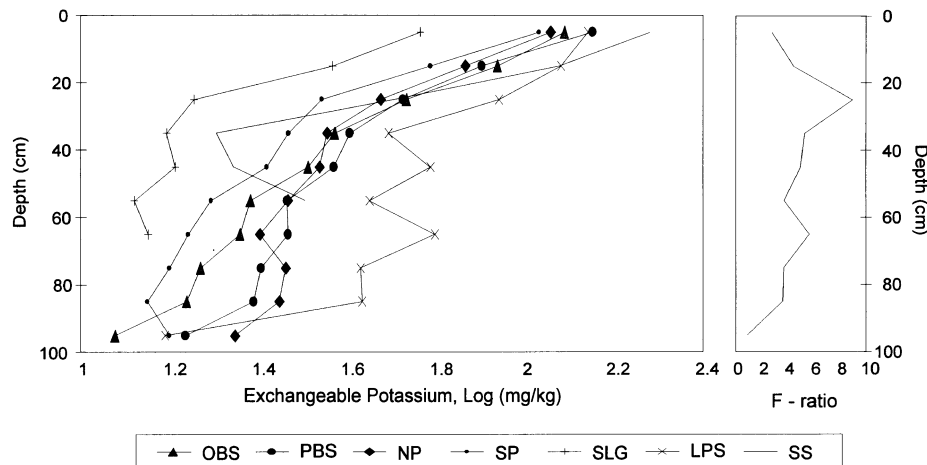


Figure 5. Vertical comparison of exchangeable potassium between seven different soil zones in Bicknoller Combe, Somerset. Total soil profiles ( $n = 64$ ); OBS (orthic brown soils,  $n = 14$ ); PBS (podzolic brown soils,  $n = 13$ ); NP (non-hydromorphic podzols,  $n = 12$ ); SP (stagnogley podzols,  $n = 13$ ); SLG (stagnogley soils,  $n = 8$ ); LPS ('lateral podzolic soils',  $n = 5$ ); SS (seepage soils,  $n = 2$ )

70 cm depths). These observations show that there is a fundamental difference in the spatial distribution of exchangeable  $K^+$  compared with some other base cations.

#### Exchangeable sodium ( $Na^+$ )

The average concentration of exchangeable  $Na^+$  is  $8.78 \text{ mg kg}^{-1}$ . Considering the general amount of dissolved  $Na^+$  in stream and rain water, the proportion held on exchangeable sites is surprisingly small. Waylen (1979) reported that  $Na^+$  is one of the most abundant cations supplied from the atmosphere and dissolved in stream water at the East Twin catchment, where the geology, vegetation and proximity to the Bristol Channel are all similar to those of the study slope. Burt (1979) reported a similarly high concentration of  $Na^+$  in throughflow water at the base of the study slope. Compared with other exchangeable bases,  $Na^+$  is barely used as a nutrient for vegetation, and its spatial mobility is mainly governed by geochemical processes (e.g. weathering and cation exchange reactions). Therefore, the low cationic proportion of exchangeable  $Na^+$  indicates that very little of the  $Na^+$  supplied from the atmosphere or from bedrock weathering is retained on soil exchange sites, and that most is freely released into the stream water during storm events.

The soil profile data show that exchangeable  $Na^+$  decreases rapidly down to a depth of 30–40 cm, below which similar levels are sustained (Figure 7). The F-ratios indicate little difference in exchangeable  $Na^+$  between the soil zones, except for seepage soils and stagnogley soils (Table II). Like the divalent cations, exchangeable  $Na^+$  is present in extremely high concentrations in seepage soils. On the other hand, stagnogley soils have the lowest concentrations throughout their depth. The correlation coefficient of exchangeable  $Na^+$  with the exchangeable divalent cations ( $Ca^{2+}$  and  $Mg^{2+}$ ) is 0.72 ( $p < 0.01$ ), and with exchangeable  $K^+$  is 0.50 ( $p < 0.01$ ). This shows that its behaviour on the slope is closer to that of divalent cations than that of the exchangeable  $K^+$ .

The distribution of exchangeable  $Na^+$  is generally uniform over the slope, with two exceptions (Figure 8). Firstly, soils on the interfluvium and upper shoulder slope, where active stagnogley soils occur, show low exchangeable  $Na^+$  level throughout their depth. As depth increases, the low levels of exchangeable  $Na^+$  seem to extend down towards the base of the slope. Secondly, the lower hollow, where throughflow converges and the saturated wedge is present, has an extremely high level of exchangeable  $Na^+$ . This feature clearly indicates that the  $Na^+$  leached from upslope accumulates in the lower hollow – the same mechanism used to explain the spatial distribution of exchangeable  $Ca^{2+}$ .

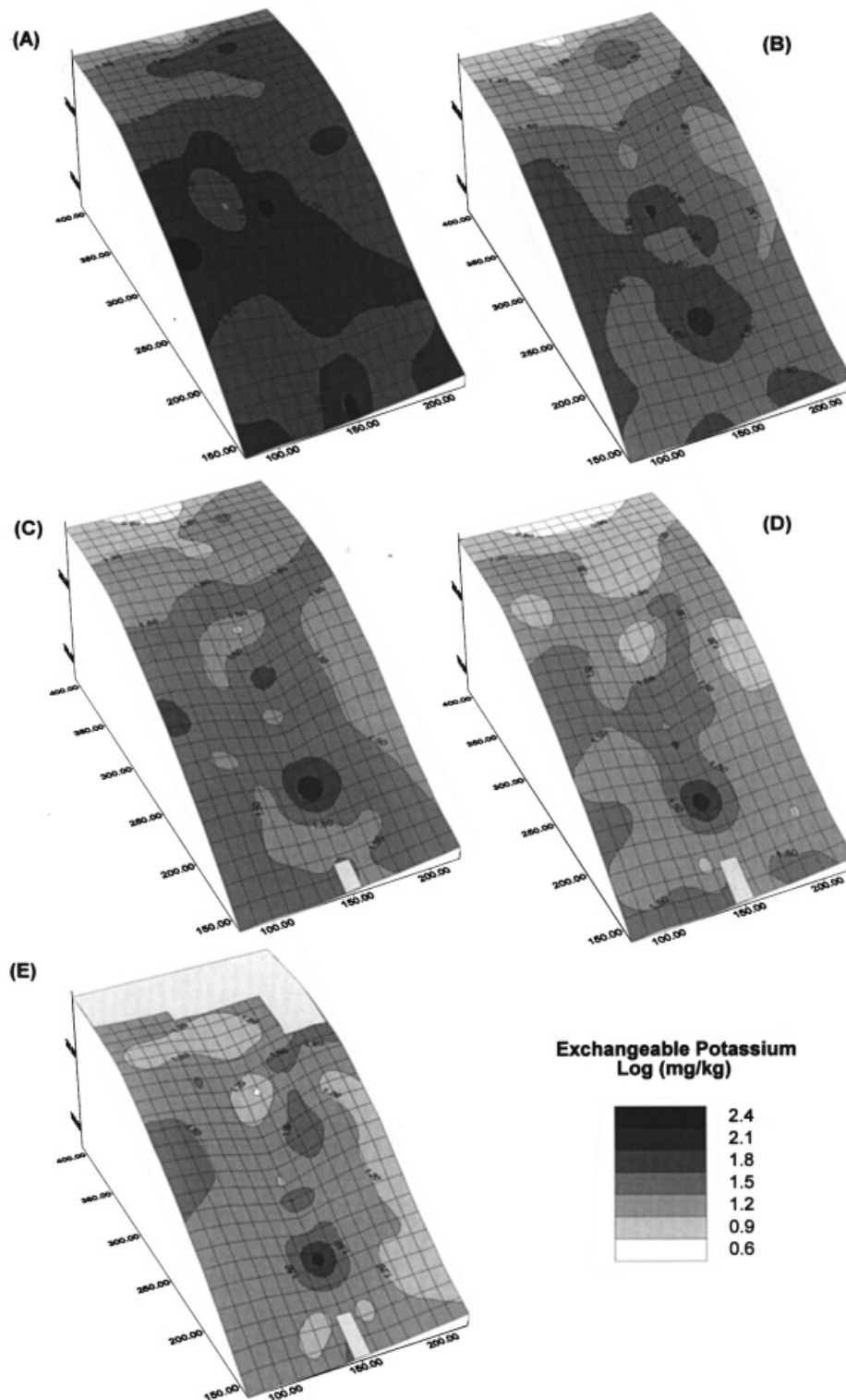


Figure 6. Spatial interpolation of exchangeable potassium in five soil layers in Bicknoller Combe, Somerset. (A) 0–10 cm depth ( $n = 64$ ); (B) 20–30 cm depth ( $n = 64$ ); (C) 40–50 cm depth ( $n = 62$ ); (D) 60–70 cm depth ( $n = 59$ ); (E) 80–90 cm depth ( $n = 48$ )

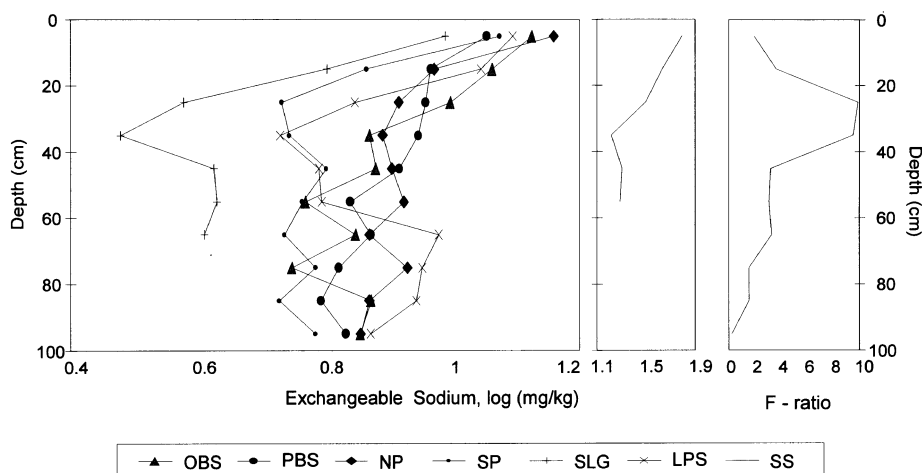


Figure 7. Vertical comparison of exchangeable sodium between seven different soil zones in Bicknoller Combe, Somerset. Total soil profiles ( $n = 64$ ); OBS (orthic brown soils,  $n = 14$ ); PBS (podzolic brown soils,  $n = 13$ ); NP (non-hydromorphic podzols,  $n = 12$ ); SP (stagnogley podzols,  $n = 13$ ); SLG (stagnogley soils,  $n = 8$ ); LPS ('lateral podzolic soils',  $n = 5$ ); SS (seepage soils,  $n = 2$ )

#### DISCUSSION: POSSIBLE LINKS BETWEEN SLOPE SOILS AND THE STREAM

The spatial distribution of exchangeable bases discussed above may illustrate the hydrochemical connection from slope soils to the stream, even though quantifying an input–output balance and detailed hydrochemical processes would be difficult to achieve. The hydrological processes operating on the study slope have already been fully documented (Burt, 1978, 1979; Anderson and Burt, 1978; Stott and Burt, 1997). Two separate stream discharge peaks occur in sequence, when there is a large rainfall event at times of low soil moisture deficit. The first discharge peak occurs very soon after rainfall, mainly due to a combination of infiltration-excess overland flow from a footpath, saturation-excess overland flow from a small marshy headwater area, and increased throughflow discharge caused by the growth of the saturated zones within the hillslope hollows. After the first peak, stream discharge declines rapidly, but then rises again to form a second 'rounded' peak one to three days after the rainfall event. This second peak is caused by throughflow alone and the delay is due to the time taken for rainwater to infiltrate into the soil and then flow downslope to the stream. The spatial behaviour of soil water potential shows that the saturated wedge at the base of the hollow expands rapidly during rainfall. The second peak in stream discharge is accompanied by deepening of the saturated wedge in the lower section of the hollow. This is due to the convergent movement of throughflow into the lower hollow from the adjacent spurs and from the upper hollow (Anderson and Burt, 1978). The long-term presence of a saturated wedge is confirmed by the spatial arrangement of gleyic orthic brown soils and the seepage soils (Figure 1).

There has been no direct assessment of the total chemical budget of the study slope, and measurements of base cations in stream water and throughflow have concentrated on short-period storm events (Burt, 1979). In order to assess the relative release rate of base cations from slope soils to the stream, a simple comparison has been made between the average concentration of exchangeable bases in slope soils and the concentration in the stream water during the storm of 14 September 1976 (as reported in Burt, 1979) (Table III). The chemograph of stream water for the storm of 14 September 1976 shows that  $\text{Ca}^{2+}$  ranged from 9 to 15  $\text{mg l}^{-1}$ ,  $\text{Na}^{+}$  ranged from 7 to 13  $\text{mg l}^{-1}$ ,  $\text{Mg}^{2+}$  ranged from 2 to 4  $\text{mg l}^{-1}$ , and  $\text{K}^{+}$  ranged from 1 to 9  $\text{mg l}^{-1}$ . The data listed in Table III allow an approximation of the amount of each base cation fixed at soil exchangeable sites relative to the amount released to the stream to be calculated, defined here as 'retention ratio'.

The retention ratios for exchangeable bases increase as follows:  $\text{Na}^{+} < \text{Ca}^{2+} = \text{Mg}^{2+} < \text{K}^{+}$ . As expected,  $\text{Na}^{+}$  supplied by atmospheric deposition and chemical weathering is poorly retained on exchangeable sites (the average retention ratio is only 0.18). Despite great differences in absolute concentrations in both soil and

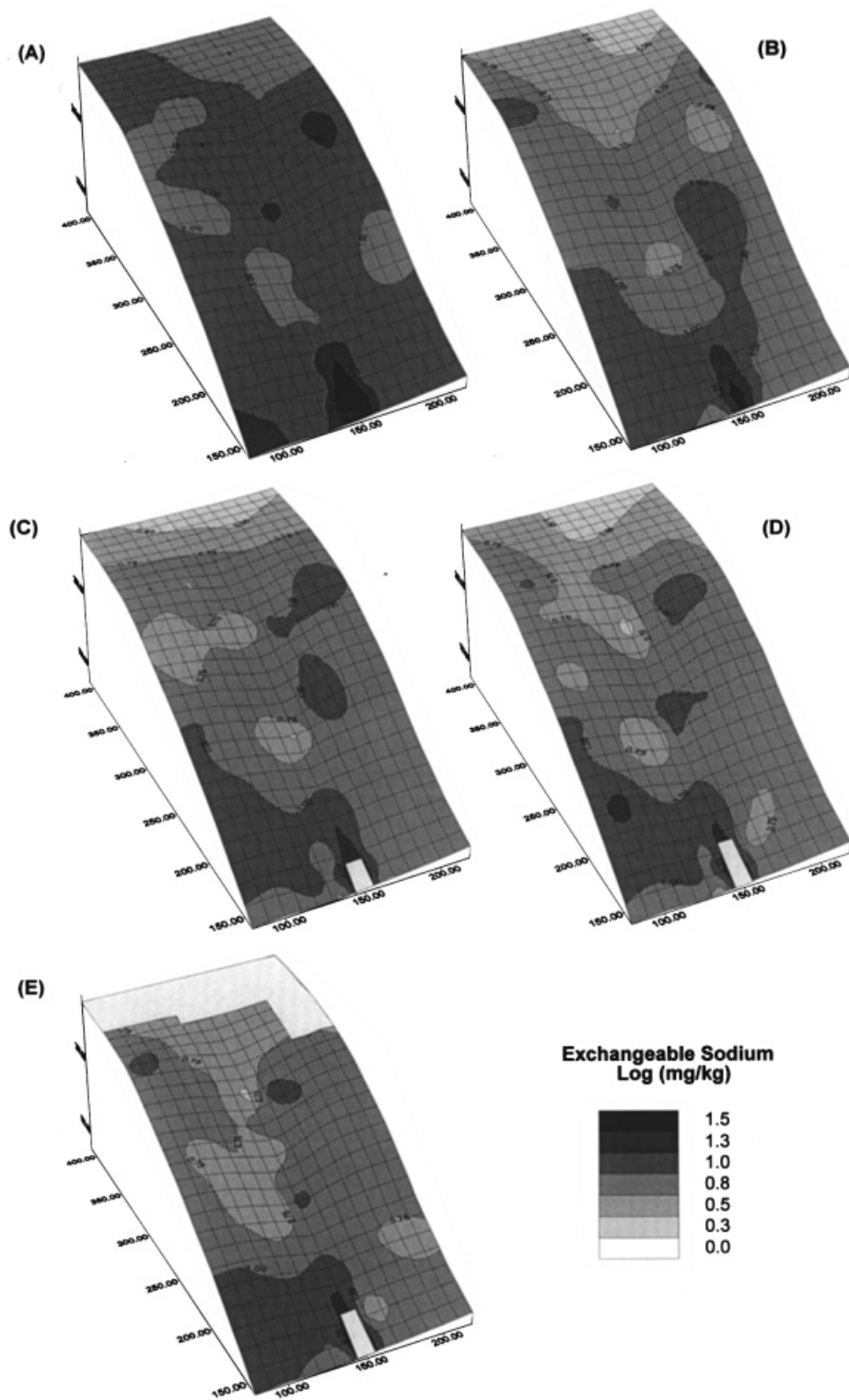


Figure 8. Spatial interpolation of exchangeable sodium in five soil layers in Bicknoller Combe, Somerset. (A) 0–10 cm depth ( $n = 64$ ); (B) 20–30 cm depth ( $n = 64$ ); (C) 40–50 cm depth ( $n = 62$ ); (D) 60–70 cm depth ( $n = 59$ ); (E) 80–90 cm depth ( $n = 48$ )

Table III. An assessment of base cation release rate from slope soils to the stream in Bicknoller Combe, Somerset

Elements	Average concentration in soils (mg kg <sup>-1</sup> ) (A)*	Concentration in stream water (mg l <sup>-1</sup> ) (B)†	Retention ratio (A)/(B)	Range
Ca <sup>2+</sup>	87.02	9–15	7.25	5.80–9.67
Mg <sup>2+</sup>	23.54	2–4	7.84	5.89–11.77
Na <sup>+</sup>	8.78	7–13	0.88	0.68–1.25
K <sup>+</sup>	50.70	1–9	10.14	5.63–50.70

\* Average concentration of exchangeable cations

† Direct reading from a chemograph of the stream water for the storm of 14 Sept. 19: 76 (from Burt, 1979).

stream water, the retention ratio of Ca<sup>2+</sup> and Mg<sup>2+</sup> is similar (7.25 for Ca<sup>2+</sup> and 7.84 for Mg<sup>2+</sup>), providing further evidence for their similar behaviour on the study slope. The retention ratio of K<sup>+</sup> is the highest of the four base cations (10.14), indicating that K<sup>+</sup> is more closely retained in the soil than any other base cation. While the general adsorption affinity of K<sup>+</sup> to exchangeable sites is slightly lower than those of higher-valent cations (Al<sup>3+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>), K<sup>+</sup> is favoured by some clay minerals, such as illite and vermiculite, and can sometimes be closely held on exchangeable sites (Hem, 1970).

In the hydrochemical response of the stream, Ca<sup>2+</sup>, Mg<sup>2+</sup> and Na<sup>+</sup> in stream water show rather similar behaviour (Burt, 1979). During the period of storm runoff, they show marked dilution in the stream, but very little change in throughflow; the dilution of stream water is due to input of overland flow, which has little time to acquire solutes from soil. During the delayed throughflow peak, the cation concentrations of both soil and stream water increase. The highest concentrations coincide exactly with the maximum extension of the saturated wedge in the centre of the hollow. These observations led Burt (1979) to the conclusion that when the rising water table came into contact with soil which had been previously unsaturated, a store of soluble weathering products produced since the last period of saturation would be available for rapid flushing into the stream. This research has established that there is a high level of divalent cations in the soils of the lower hollow, providing a ready supply for leaching by throughflow.

The hydrochemical response of K<sup>+</sup> differs from that of other base cations described above. While other base cations are diluted during stormflow mainly due to overland flow, the concentration of K<sup>+</sup> is increased. Furthermore, while the concentration of other base cations increases during the delayed peak in stream discharge caused by throughflow, that of K<sup>+</sup> generally does not: an increase in K<sup>+</sup> in throughflow and stream water is only observed in the largest delayed hydrographs when the saturated wedge extends to the base of the spurs (Burt, 1979). This unusual response of K<sup>+</sup> has been observed in many other studies, recently summarized by Stott and Burt (1997). The spatial distribution of exchangeable K<sup>+</sup> examined in this research may provide a key to understanding the hydrochemical response behaviour of K<sup>+</sup>. Compared to other base cations, soils in the lower hollow, including the seepage soils, and the orthic brown soils have a lower level of exchangeable K<sup>+</sup>. On the other hand, the base of the spurs and the hollow above the seepage soil zones have a relatively high level of exchangeable K<sup>+</sup>. In relation to the leaching mechanism proposed by Burt (1979), the relatively low exchangeable K<sup>+</sup> concentration at the base of the slope, especially around the seepage soils, would give little chance for K<sup>+</sup> to be acquired from soils by a rising saturated wedge. However, when the amount of throughflow water increases, the expansion of the saturated wedge upslope allows additional K<sup>+</sup> to be leached from upslope soils where a higher level of exchangeable K<sup>+</sup> exists.

One question arising from this examination of exchangeable K<sup>+</sup> is why there are low levels in the hollow. This pattern contradicts the increase in other base cations on the same part of the slope, and possibly indicates that exchangeable K<sup>+</sup> is depleted under water saturation. The behaviour of K<sup>+</sup> seems to parallel that of Al<sup>3+</sup>, which also shows clear depletion in the water-saturated parts of the base of the slope (see Park and Burt, 1999). The depletion of exchangeable Al<sup>3+</sup> in the saturated wedge is explained by rapid cation exchange with divalent base cations in throughflow, a mechanism which directly accounts for the rapid rise in Al<sup>3+</sup> concentration in the early stage of storm peaks. One possible explanation for the depletion of K<sup>+</sup> may be the similar mechanism with Al<sup>3+</sup>. The rapid replacement of K<sup>+</sup> by added divalent cations is a well established

cation exchange reaction (Mehlich and Reed, 1945). In a  $K^+$  leaching experiment using distilled water and calcium sulphate solution, Mehlich and Reed (1945) observed that the rate of loss of  $K^+$  was greater when calcium sulphate was first added; losses of  $K^+$  were then very much smaller and virtually independent of further calcium sulphate additions. The application of this concept to potassium leaching at the catchment scale may be an interesting line of enquiry to understand the hydrochemical behaviour of  $K^+$ , in addition to the processes specified in Stott and Burt (1997).

## CONCLUSION

The exchangeable base cations considered in this research show different spatial distributions on the slope due to their differing involvement in nutrient cycles, chemical weathering and exchangeable reactions. The exchangeable base cations show high total variability. In general, however, their total variance is controlled mainly by vertical differences but with some additional influence of lateral catenary distribution processes.  $K^+$  shows the clearest vertical difference over the slope, and is followed by  $Ca^{2+}$  and  $Mg^{2+}$ , then  $Na^+$ . In a nutrient-poor heathland environment, the spatial distribution of major nutrient cations, such as  $Ca^{2+}$ ,  $Mg^{2+}$  and  $K^+$ , is tightly controlled by the soil-vegetation system, which results in a homogeneous topsoil right across the slope. Complex catenary processes barely influence the spatial distribution of these nutrient base cations in the surface mineral soil layers.  $Na^+$  is an exception to this vegetation-controlled spatial distribution, because of its minimal involvement in nutrient cycling. Only small amounts of  $Na^+$  supplied by atmospheric input and bedrock weathering are stored in the soil, and its spatial distribution is mainly controlled by hydrochemical processes. In subsurface soil, cations liberated from topsoil become subject to catenary redistribution over the hillslope according to the hydrological flowpaths (throughflow), and are eventually released into the stream.

The saturated wedge developed at the base of the slope plays a key role in the storage and release of nutrient cations.  $Ca^{2+}$ ,  $Mg^{2+}$  and  $Na^+$  carried by throughflow are stored in the saturated wedge and gradually released into the stream with the rise of the saturation wedge during storm events.  $K^+$ , however, shows apparently different spatial characteristics with a deficit in the saturated wedge. It is hypothesized that cation exchange reactions involving the divalent cations and  $Na^+$  have removed potassium from exchange sites within the saturation wedge, but this idea needs further study both in the field and under controlled conditions in the laboratory.

## REFERENCES

- Amacher, M. C., Henderson, R. E., Breithaupt, M. D., Seale, C. L. and LaBauve, J. M. 1990. 'Unbuffered and buffered salt methods for exchangeable cations and effective cation-exchange capacity', *Soil Science Society of America Journal*, **54**, 1036–1042.
- Anderson, M. G. and Burt, T. P. 1978. 'The role of topography in controlling throughflow generation', *Earth Surface Processes*, **3**, 331–344.
- Ball, D. F. and Williams, W. M. 1968. 'Variability of soil chemical properties in two uncultivated brown soils', *Journal of Soil Science*, **19**, 379–391.
- Beckett, P. H. T. and Webster, R. 1971. 'Soil variability: A review', *Soils and Fertilizers*, **34**, 1–15.
- Billett, M. F. and Cresser, M. S. 1992. 'Predicting stream-water quality using catchment and soil chemical characteristics', *Environmental Pollution*, **77**, 263–269.
- Burt, T. P. 1978. Runoff Processes in A Small Upland Catchment with Special Reference to the Role of Hillslope Hollows, Unpublished PhD Thesis, University of Bristol.
- Burt, T. P. 1979. 'The relationship between throughflow generation and the solute concentration of soil and stream water', *Earth Surface Processes*, **4**, 257–266.
- Burt, T. P. 1986. 'Runoff processes and solutational denudation rates on humid temperate hillslopes', in Trudgill, S. T. (Ed.), *Solute Processes*, John Wiley & Sons, Chichester, 195–250.
- Chappell, N. and Ternan, L. 1992. 'Flow path dimensionally and hydrological modelling', *Hydrological Processes*, **6**, 327–345.
- Cleaves, E. T., Godfrey, A. E. and Bricker, O. P. 1970. 'Geochemical balance of a small watershed and its geomorphic implication', *Geological Society of America Bulletin*, **81**, 3015–3032.
- Crabtree, R. W. and Burt, T. P. 1983. 'Spatial variation in solutational denudation and soil moisture over a hillslope hollow', *Earth Surface Processes and Landforms*, **8**, 151–160.
- Duchaufour, Ph. 1982. *Pedology: Pedogenesis and Classification*, (translated by T. R. Paton), George Allen and Unwin, London.
- Edmonds, E. A. and Williams, B. J. 1985. *Geology of the Country around Taunton and the Quantock Hills*, Memoir for 1:50,000 Geological Sheet 295, New Series, British Geological Survey, London.
- Frankland, J. C. 1976. 'Decomposition of bracken litter', *Botanical Journal of the Linnean Society*, **73**, 133–143.



- Furrer, G., Westall, J. and Sollins, P. 1989. 'The study of soil chemistry through quasi-steady-state models: I. Mathematical definition of model', *Geochimica et Cosmochimica Acta*, **53**, 595–601.
- Gimingham, C. H. 1972. *Ecology of Heathlands*, Chapman and Hall, London.
- Hem, J. D. 1970. Study and interpretation of the chemical characteristics of natural water, US Geological Survey Water Supply Paper, No. 1473.
- Hill, A. R. 1990. 'Groundwater concentrations in the riparian zone of a forested headwater stream', *Hydrological Processes*, **4**, 121–130.
- Hoosbeek, M. R. and Bryant, R. B. 1992. 'Toward the quantitative modeling of pedogenesis—a review', *Geoderma*, **55**, 183–210.
- Johnston, N. M., Likens, G. E., Bormann, F. H., Fisher, D. W. and Pierce, R. S. 1969. 'A working model for the variation in stream water chemistry of the Hubbard Brook experimental forest in New Hampshire', *Water Resources Research*, **5**, 1353–1363.
- Mehlich, A. and Reed, J. F. 1945. 'The influence of degree of saturation, potassium level, and calcium additions on removal of calcium, magnesium, and potassium', *Soil Science Society of America Proceedings*, **10**, 87–93.
- Milliken, G. A. and Johnson, D. E. 1984. *Analysis of Messy Data, Vol. 1, Designed Experiments*, Lifetime Learning Publication, Belmont, CA.
- Moore, I. D., Grayson, R. B. and Ladson, A. R. 1993. 'Digital terrain modelling: A review of hydrological, geomorphological, and biological applications,' in Beven, K. J. and Moore, I. D. (Eds), *Terrain Analysis and Distributed Modelling in Hydrology*, John Wiley & Sons, Chichester, 7–34.
- Mulder, J., Pijpers, M. and Christophersen, N. 1991. 'Water flow paths and the spatial distribution of soils and exchangeable cations in an acid rain-impact and a pristine catchment in Norway', *Water Resource Research*, **27**, 2919–2928.
- Paces, T. 1986. 'Rates of weathering and erosion derived from mass balance in small drainage basins', in Colman, S. M. and Dethier, D. P. (Eds), *Rates of Chemical Weathering of Rocks and Minerals*, Academic Press, Orlando, 467–502.
- Park, S. J. 1997. *Modelling Soil-Landform Continuum on a Three-Dimensional Hillslope*, unpublished D.Phil thesis, University of Oxford.
- Park, S. J. and Burt, T. P. 1999. 'The distribution of solute processes on an acid hillslope and the delivery of solutes to a stream: II. Exchangeable  $\text{Al}^{3+}$ ', *Earth Surface Processes and Landforms* (in press).
- Park, S. J., Burt, T. P. and Bull, P. A. 1996. 'A soil–landscape continuum on a three-dimensional hillslope, Quantock Hills, Somerset', in Anderson M. G. and Brooks S. M. (Eds), *Advances in Hillslope Processes, Volume 1*, John Wiley & Sons, Chichester, 367–396.
- Stott, R. E. and Burt, T. P. 1997. 'Potassium chemistry of a small upland stream following a major drought', *Hydrological Processes*, **11**, 189–201.
- Trudgill, S. T. 1986. 'Solute processes and landforms: an assessment,' in Trudgill, S. T. (Ed.), *Solute Processes*, John Wiley & Sons, Chichester, 497–509.
- Trudgill, S. T. 1988. *Soil and Vegetation System*, Clarendon Press, Oxford.
- Trudgill, S., Ball, J. and Rawlins, B. 1996. 'Modelling the solute uptake components of hillslope hydrochemistry: Are flow times and path lengths important during mineral dissolution', in Anderson, M. G. and Brooks, S. M. (Eds), *Volume 1, Advances in Hillslope Processes*, John Wiley & Sons, Chichester, 295–324.
- Waylen, M. J. 1979. 'Chemical weathering in a drainage basin underlain by Old Red Sandstone', *Earth Surface Processes*, **4**, 167–178.
- Wilding, L. P. 1984. 'Spatial variability: its documentation, accommodation and implication to soil surveys,' in Nielsen, D. R. and Bouma, J. (Eds), *Soil Spatial Variability*, Pudoc, Wageningen, 166–193.
- Williams, A. G., Kent, M. and Ternan, J. L. 1987. 'Quantity and quality of bracken throughfall, stemflows, and litterflow in a Dartmoor catchment', *Journal of Applied Ecology*, **24**, 217–230.